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EXPLOSIBILITY TESTS ON REFERENCE SULPHIDE MINERAL SAMPLES

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EXPLOSIBILITY TESTS ON MSL REFERENCE SULPHIDE MINERAL SAMPLES

by

K.J. Mintz*

ABSTRACT

In order to determine the hazards of handling reference materials generated from ores containing high concentrations of pyrrhotite, explosion tests were carried out in the 20-L vessel. The minimum explosible concentration of WMS-1 (which contains about 65% pyrrhotite) was 820 g/m^3, and of RTS-4 (which contains about 90% pyrrhotite) was 340 g/m^3. The maximum explosion pressure was about 220 - 240 kPa, with the maximum rate of pressure rise about 2000 - 2500 kPa/s. The minimum ignition energies of WMS-1 and RTS-4 were roughly 3.5 and 2 kJ, respectively. The minimum ignition temperatures, measured in the Godbert-Greenwald furnace, were 520 and 530°C, respectively. In addition, both samples were found not to fall under the "flammable solids" classification of WHMIS.

In summary, although the hazard of these reference materials is low compared to most other combustible dusts, it is recommended that reasonable care be taken to prevent energetic sources of ignition from contacting the dust and that the dust be kept away from very hot surfaces.

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CONTRÔLE DE LA LIMITE D'EXPLOSIBILITÉ DES ÉCHANTILLONS DE MINÉRAUX SULFURÉS DE RÉFÉRENCE, PRÉSENTÉS PAR LES LABORATOIRES DES SCIENCES MINÉRALES (LSM)

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RÉSUMÉ

On a mené des essais au moyen d'un récipient de 20 L afin de déterminer les risques d'explosion associés à la manutention des matériaux de référence obtenus à partir de minerais à haute teneur en pyrrhotine. Il y a risque d'explosion quand la concentration minimale de WMS-1 (dont la teneur en pyrrhotine est d'environ 65 %) est de 820 g/m^3, et quand la concentration minimale de RTS-4 (dont la teneur en pyrrhotine est d'environ 90 %), est de 340 g/m^3. La pression maximale d'explosibilité était d'à peu près 220 à 240 kPa à une pression maximale croissante de 2 000 à 2 500 kPa/s. Les températures minimales d'inflammabilité de WMS-1 et de RTS-4 étaient d'à peu près 3,5 et 2 kJ, respectivement. Les températures minimales d'inflammabilité de la chaudière Godbert-Greewald, telles que mesurées, étaient de 520 à 530°C, respectivement. De plus, on s'est rendu compte que les deux échantillons n'étaient pas classés dans la catégorie "solides inflammables" par la Système d'information sur les matières dangereuses utilisées au travail (SIMDUT).

En définitive, bien que ces matériaux de référence présentent des risques d'explosion peu élevés comparativement à la plupart des autres particules combustibles, il faut s'assurer que les sources d'énergie inflammables ne soient pas en contact avec les particules et que ces dernières soient tenues à l'écart des surfaces très chaudes.

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INTRODUCTION

Under the Canadian Certified Reference Materials Project in the Mineral Sciences Laboratories (MSL), samples of ores, in the form of fine dusts, are prepared as analytical standards for the mining industry. Dust clouds of sulphide ores containing high concentrations of pyrite or pyrrhotite are known to be capable of exploding. Therefore, to ensure the safe processing of these materials, it was decided to carry out appropriate tests on the explosibility of a candidate reference material, WMS-1, and a previously-processed reference material, RTS-4. Chemical analysis was carried out by MSL and the mineralogical composition estimated by them from that data. These are shown below, along with the sieve analysis.

	WMS-1	RTS-4
Chemical analysis:		
% sulphur	30.6	35.6
elemental sulphur	--	0.4
sulphate	--	0.7
as sulphide	--	35.0
% iron	50.9	56.8
% nickel	3.8	0.9
% copper	1.3	--
% silicon	--	1.1
Mineralogical composition:		
pyrrhotite	65	90
pentlandite	10	--
chalcopyrite	3	--
iron oxides	<11	--
silicates	11	10
Sieve analysis (%)		
<400 mesh	86	86
400 - 325 mesh	12	7
325 - 200 mesh	2	6

APPARATUS

Explosion Tests

The explosion tests were carried out in a 20-L vessel designed by the U.S. Bureau of Mines (1), with minor modifications made in this laboratory (2). The consensus by experts in dust explosions is that 20-L is the minimum size of vessel that can be used to determine the explosibility of dusts. The classical Hartmann apparatus (3), which is only 1.2 L in volume, has been found to yield significant errors, particularly for dusts that have high minimum ignition energies, such as is the case for sulphide dusts (see below). A 1-m^3 vessel is in use in Europe; the logistics of using such a large vessel makes each test very expensive.

Dust explosion experts also concur that a strong ignitor, such as the 5-kJ Sobbe chemical ignitor, is required for the determination of the minimum explosible concentration (MEC). Use of a continuous electrical discharge, as was formerly used, can indicate that a dust is not explosible when indeed it is. All the explosion tests used for determination of the MEC in this study used the 5-kJ Sobbe ignitor. Weaker Sobbe ignitors were used for the determination of the minimum ignition energy.

The detailed test procedure used in this laboratory has been given elsewhere (4). Briefly, a weighed amount of dust was placed into the sample holder at the base of the vessel, the ignitor was placed in the centre of the vessel, the vessel was closed and then evacuated. A 16-L vessel was filled with air at 1300 kPa and the trigger on the control panel was pressed to start the test. A solenoid located between the 16-L vessel and the dust chamber opened for a preset time[1] which allowed the air to entrain the dust and form a reasonably homogeneous dust cloud in the 20-L vessel at a pressure of one atmosphere absolute. After another preset time[2], the ignitor fired. The entire pressure history of the test was captured on a Nicolet 4094 digital oscilloscope. After the combustion gases had cooled, they were passed through a

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[1]The time required depends primarily on the pressure used in the 16-L vessel, but also on the density and quantity of the dust being tested. The appropriate values are known from our previous tests on sulphide dusts.

[2]The appropriate value, also known from our previous work, depends on the settling rate of a cloud of the particular dust.

Beckman oxygen analyzer, from which the percentage of oxygen consumed was calculated. A fine thermocouple is installed inside the vessel, and its output was also recorded by the oscilloscope. Although a thermocouple cannot be expected to measure the actual temperature of the flame front during the explosion, it provides useful confirmation of the existence of the explosion.

The Sobbe ignitor itself generates a significant pressure (about 50 kPa for the 5kJ ignitor). This is taken into account by subtracting the pressure curve of the ignitor from the experimental pressure trace. The rate of pressure rise, $(dP/dt)_m$, is determined from the derivative curve, generated numerically by the oscilloscope.

The minimum ignition temperature (MIT) is determined by the Godbert-Greenwald furnace (5). Briefly, a small cloud of dust is blown into the top of a tubular furnace, which is open at its bottom. The MIT is the lowest temperature that flame or sparks are emitted from the bottom of the furnace.

The apparatus used for the Workplace Hazardous Materials Information System (WHMIS) method for classifying materials into Division 4 of Class B ("flammable solids") is described in Schedule V of the WHMIS Regulations. It consists of a metal boat into which the powder is packed; the powder is lit at one end with a candle.

RESULTS AND DISCUSSION

Minimum Explosible Concentration (MEC)

The MEC can be defined as the smallest concentration of dust that, once ignited, will propagate an explosion. The U.S. Bureau of Mines has proposed that the MEC can be found by finding that concentration that yields an overpressure equal to the initial pressure. For tests that are carried out at one atmosphere, as is the case with the tests reported here, the overpressure required is 101 kPa.

Figure 1 shows the overpressure as a function of the concentration for WMS-1[3]. The S-shaped curve is typical for these types of curves. Using the U.S. Bureau of Mines criterion, the MEC is 820 g/m^3. The estimated uncertainty

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[3]Open circles represent tests using the 5-kJ ignitor; the closed circle represents a test using the 2.5-kJ ignitor, which is discussed in the MIE section.

in this procedure is ± 20 g/m^3.

Figure 2 shows $(dP/dt)_m$ as a function of concentration for WMS-1. As mentioned above, the uncertainty in this parameter is much greater than for the overpressure; no value could even be estimated for the test at the lowest concentration. The maximum slope of the curve occurs approximately at the same concentration as Fig. 1.

Figure 3 shows the percentage of the original oxygen that was consumed in each test. The shape of the curve is similar to Fig. 1. The maximum slope occurs also at about 820 g/m^3. Note, however, that even at the highest concentrations, not all the oxygen was consumed. This is an indication of a relatively weakly-explosible material.

Figure 4 shows the temperature rise as a function of concentration. The ignitor alone produces a temperature rise of about 35 °C. The shape of the curve is similar to the preceding curves.

The results for RTS-4 are shown in Figs. 5 - 8, which show the same parameters and have the same scales as Figs. 1 - 4, so as to allow easy comparison. From the graph, the MEC is found to be 340 ± 20 g/m^3.

Maximum Explosion Pressure (MEP)

Figure 1 indicates that the explosion pressure will reach a constant value (the MEP) at a sufficiently high concentration. There was insufficient quantity of sample provided to allow an exact determination of the MEP. From the graph, the MEP of WMS-1 is estimated to be about 240 ± 20 kPa. Similarly, the MEP of RTS-4 is estimated from Fig. 5 to be about 220 ± 10 kPa.

The values of $(dP/dt)_m$ are rather more difficult to estimate. Very approximately, Fig. 2 yields 2000 kPa/s for WMS-1, and Fig. 6 yields 2500 kPa/s for RTS-4.

Minimum Ignition Energy (MIE)

The Sobbe ignitors are available only in 0.5, 1.0, 2.5, 5.0 and 10.0 kJ strengths. Hence, they can not be used to determine a precise value of the MIE. In Figs. 1, 3 and 4, the filled circles represent a test using a 2.5 kJ ignitor on the WMS-1. It can be seen that this energy was slightly insufficient to cause an ignition. Therefore, the MIE of WMS-1 is between 2.5 - 5.0 kJ; the best estimate would be 3.5 ± 1 kJ.

The filled circles in Figs. 5 - 8 represent tests using 1.0 and 2.5 kJ ignitors, as indicated on the graphs. The values of the parameters using the 1.0 kJ ignitor are very low, indicating that energy is considerably below the MIE. The 2.5 kJ ignitor produces values somewhat below those produced by the 5.0 kJ, indicating that it is just slightly above the MIE. Hence, the MIE of RTS-4 is estimated to be 2 ± 1 kJ.

Minimum Ignition Temperature (MIT)

With most explosible dusts, a distinct flame is observed if the temperature of the furnace is above the MIT. By contrast, no matter how high the temperature of the furnace is, sulphide ore dusts produce only sparks, the quantity increasing steadily with increasing temperature. Some authorities consider observation of sparks not to be an indicator of ignition. From that viewpoint, clouds of sulphide dusts will not ignite at all up to 900 °C, the maximum temperature of the furnace. In this writer's opinion, this is unreasonable. It is recommended that the MIT for sulphide dusts be defined as the lowest temperature that sparks are observed.

Using the "spark" criterion, the MIT of WMS-1 was measured as 520 ± 10 °C, that of RTS-4, 530 ± 10 °C. Within experimental error, they are the same.

WHMIS Tests

The WHMIS test on WMS-1 did not ignite the dust, but only produced very slight charring of the surface which had been exposed to the flame. The RTS-4 also did not ignite, but did generate some red dust on the surface which had been exposed to the flame. This dust must be, of course, Fe_2O_3. Hence, both materials easily pass the WHMIS test for flammable solids, and therefore, do not fall under Division 4 of Class B of the WHMIS regulations. It should be noted that tests were not carried out on the dusts' propensity to spontaneous combustion (Division 6 of Class B of WHMIS).

The United Nations has published recommendations on transportation of dangerous goods. Division 4.1 (c) is the classification for readily-combustible solids. The requirements are much more stringent than for WHMIS. For a preliminary screening, the test is somewhat similar to the WHMIS test, but a gas burner with a minimum temperature of 1000 °C is applied for 2 minutes,

instead of a candle applied for 5 s. The RTS-4 did not ignite in this test, but produced a slight amount of smoke and a thicker layer of red dust was produced in the area exposed to the flame. Hence, from the viewpoint of the transportation of dangerous goods, these dusts would not be considered to be readily-combustible.

CONCLUSIONS

The RMS-4 has a much smaller MEC than WMS-1, because it contains a higher percentage of pyrrhotite. Very few combustible dusts have values of MEC as great as WMS-1; the majority (e.g. coals, plastics, starch) have MEC's <100 g/m^3 (6).

Similarly, the MEP's of both RMS-4 and WMS-1 are much smaller than those found for most combustible dusts, which are usually in the range 500 - 900 kPa (6). The rates of pressure rise are also much smaller than those of other combustible dusts.

On the other hand, the MIT's of RMS-4 and WMS-1 are in the normal range for combustible dusts, though the comparison may be clouded by the fact that only sparks were observed.

The tests showed that these dusts are not classified as flammable solids under either WHMIS or transportation of dangerous goods. However, it is recommended that spontaneous combustion tests be carried out on these dusts, since pyrrhotite is known to be pyrophoric.

The MIE of both RMS-4 and WMS-1 are very high. According to Field (6), static electrical discharges are only hazards for dusts having an MIE of less than 50 mJ, which is definitely not the case here.

In summary, although the hazard of these reference materials is low compared to most other combustible dusts, it is recommended that reasonable care be taken to prevent energetic sources of ignition from contacting the dust and that the dust be kept away from very hot surfaces.

ACKNOWLEDGEMENTS

The data in Table 1 was supplied by Dr. Clint Smith of the Mineral Sciences Laboratories.

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Fig.1. Explosion Pressure vs. Concentration

Mineral Sciences Laboratories MMS-1

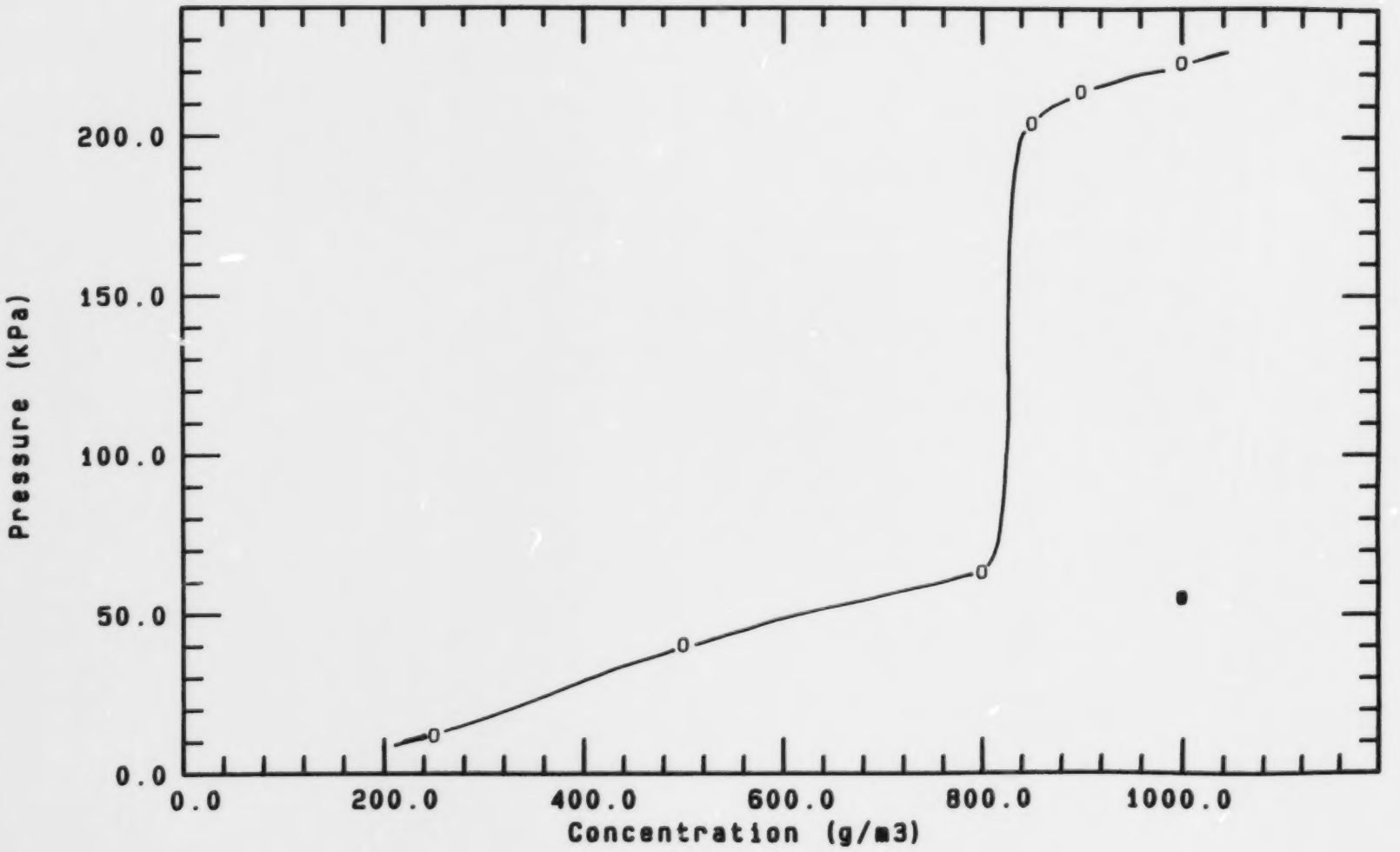
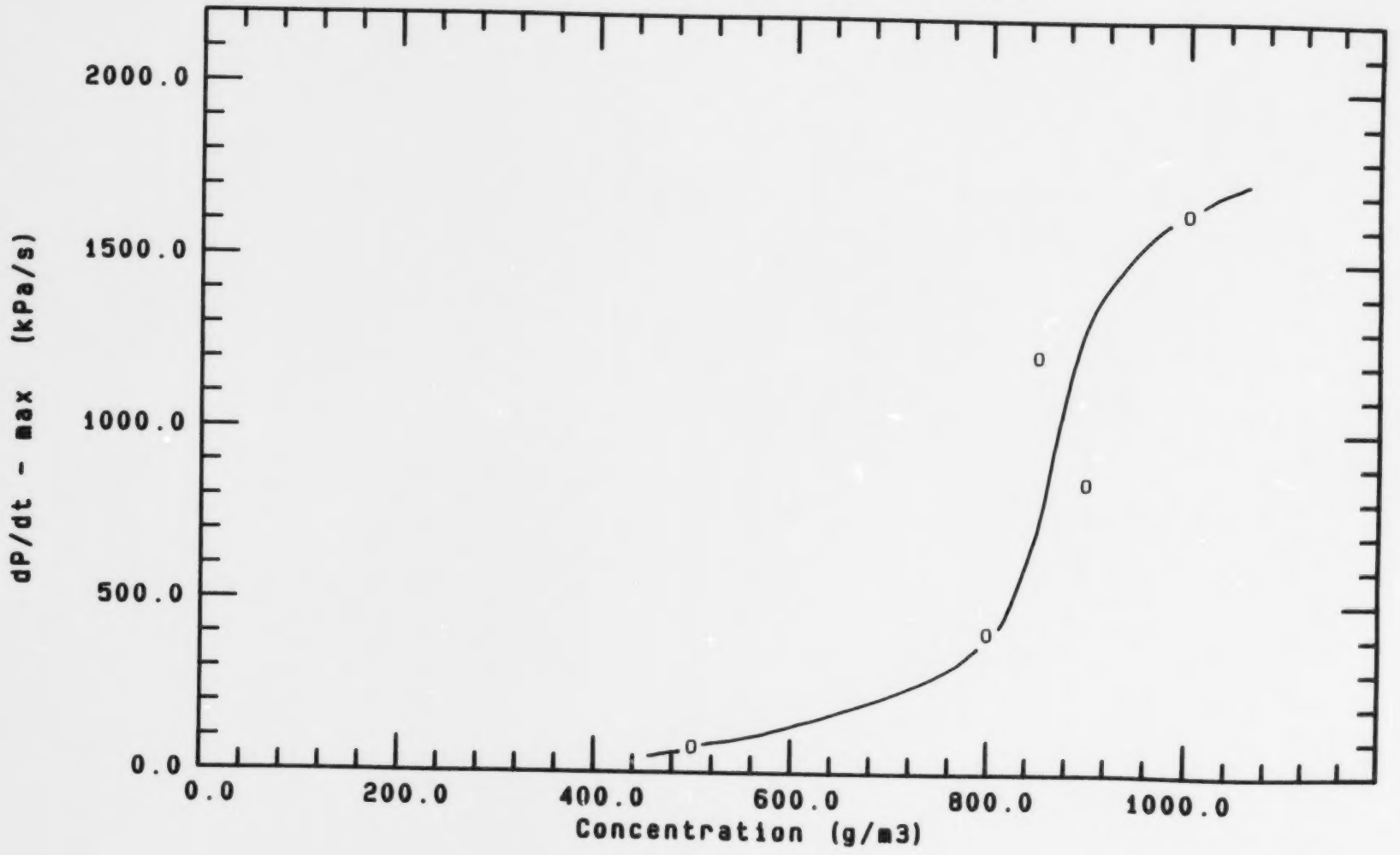


Fig.2. Rate of Pressure Rise vs. Concentration

Mineral Sciences Laboratories WMS-1



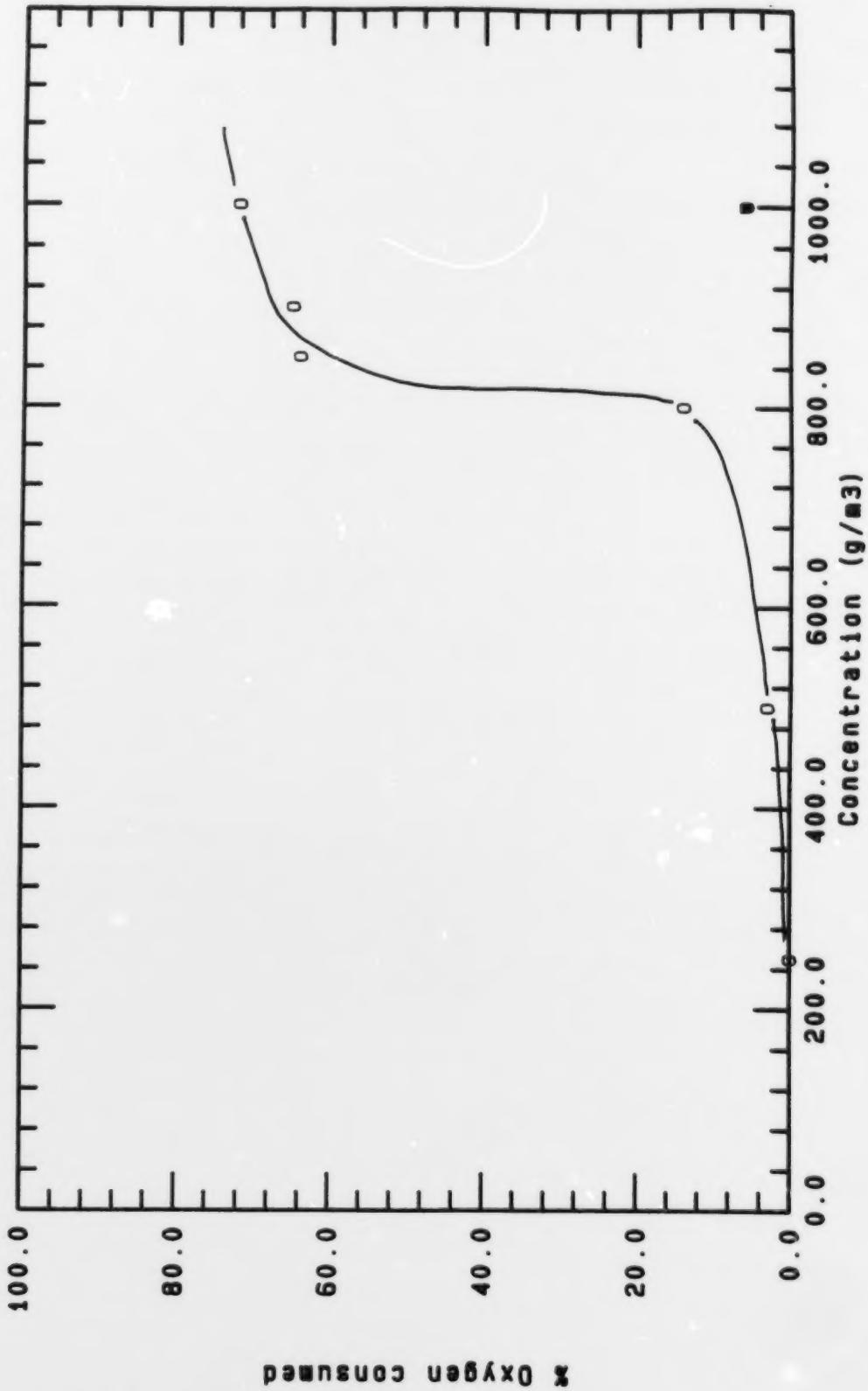


Fig.3. Oxygen Consumption vs. Concentration

Mineral Sciences Laboratories MMS-1

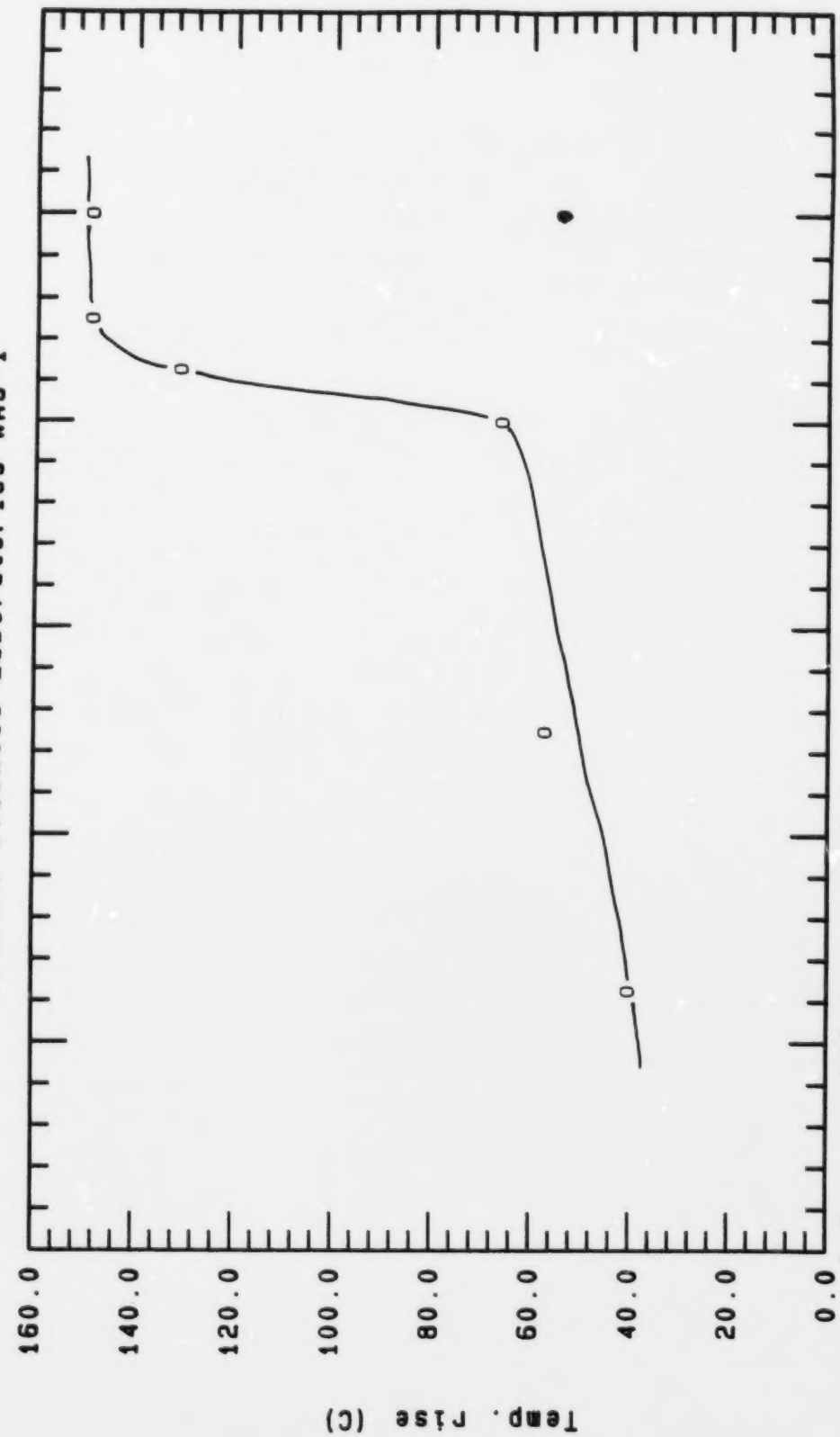


Fig.4. Temperature Rise vs. Concentration

Mineral Sciences Laboratories WMS-1

Fig.5. Explosion Pressure vs. Concentration

Mineral Sciences Laboratories RTS-4

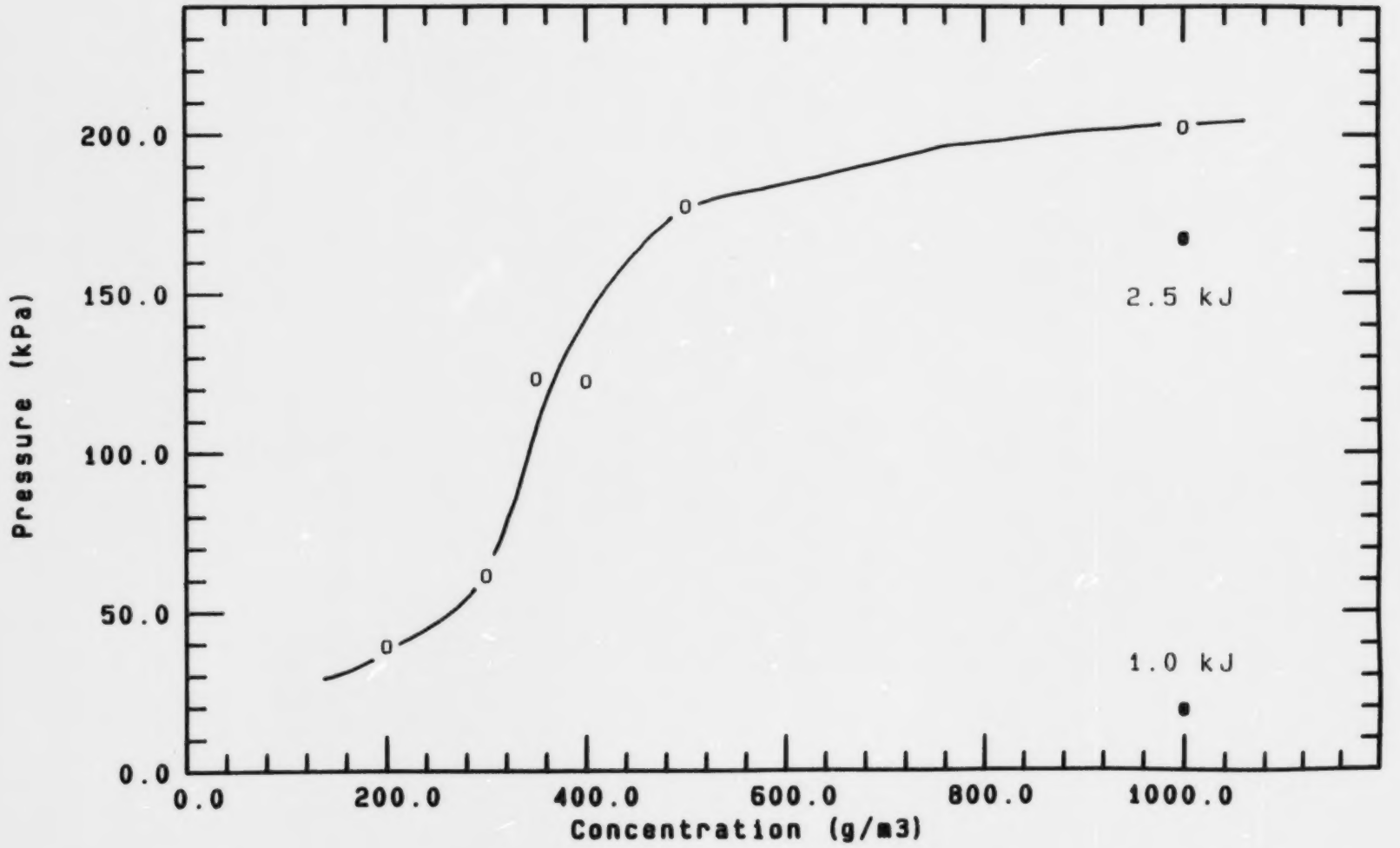
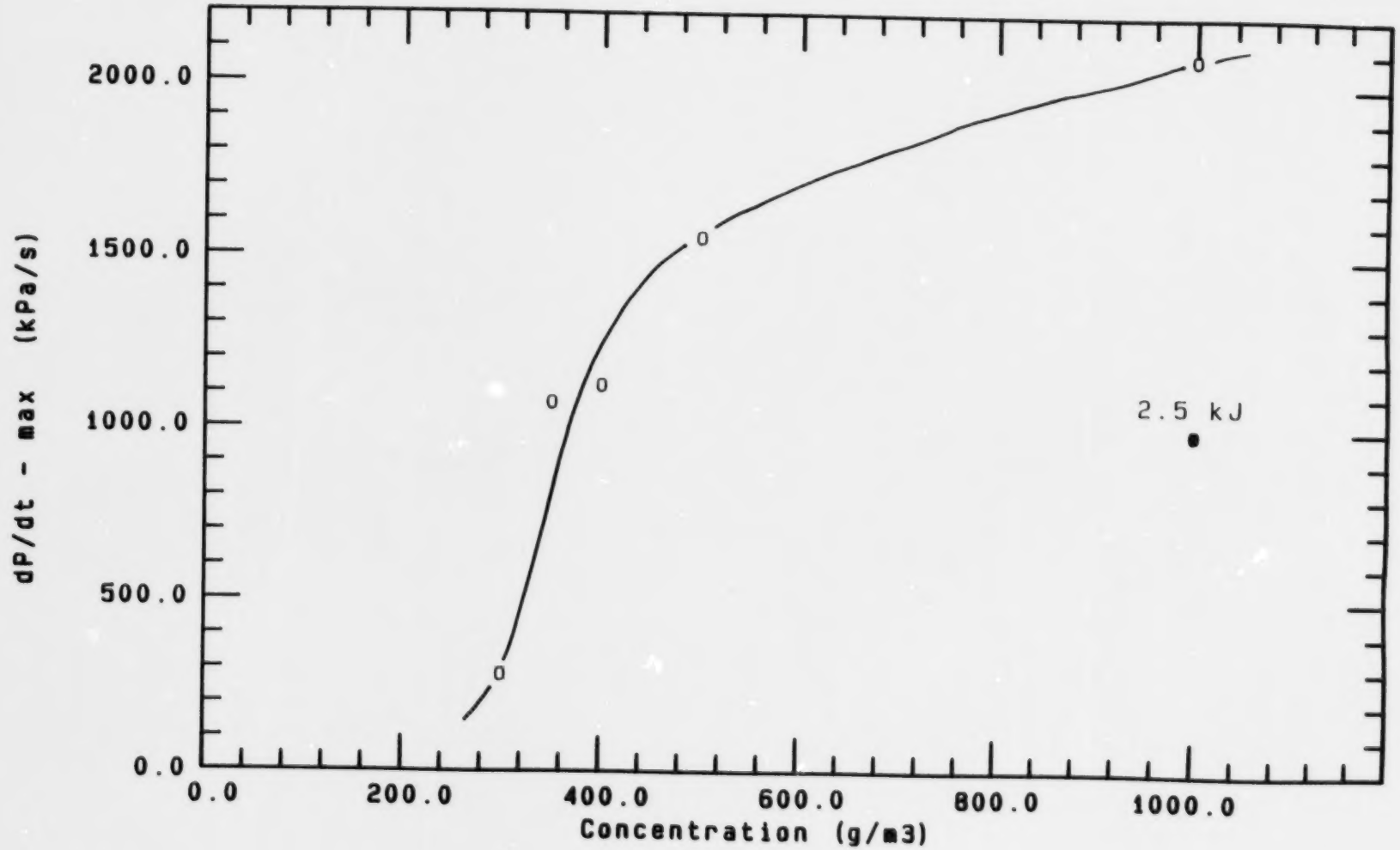


Fig.6. Rate of Pressure Rise vs. Concentration

Mineral Sciences Laboratories RTS-4



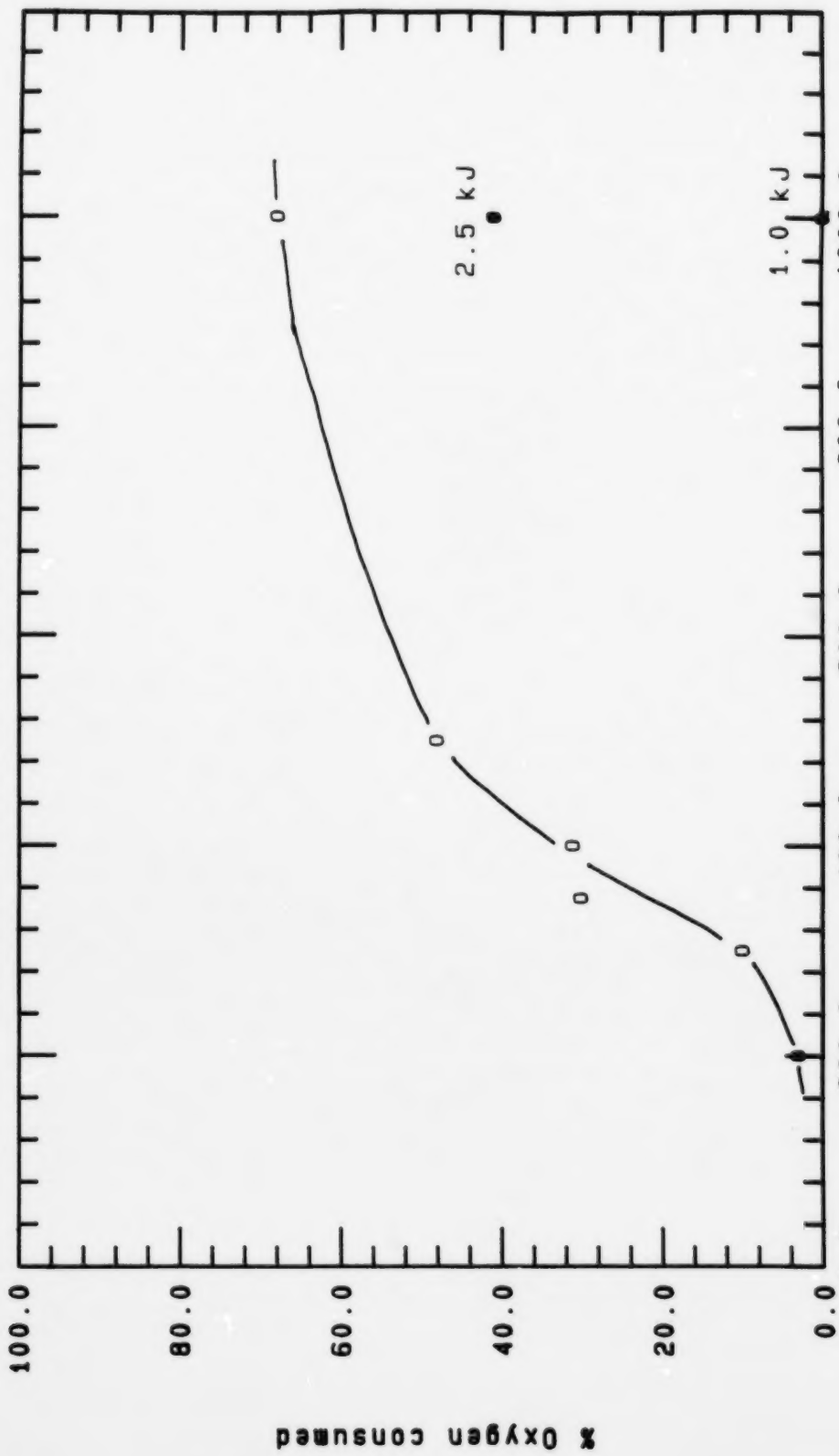


Fig.7. Oxygen Consumption vs. Concentration

Mineral Sciences Laboratories ATS-4

Fig.8. Temperature Rise vs. Concentration

Mineral Sciences Laboratories RTS-4